

Energetic of nitrogen incorporation reactions in SiO₂

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We study using first-principles calculations the energetic, structural and electronic properties of nitrogen incorporation in SiO₂. We consider NO, NH, N₂ and atomic N as the nitriding species interacting with a Si–Si bond of an otherwise perfect SiO₂ network in order to simulate the nitrogen incorporation near Si–SiO₂ interface regions. We find that all the species react with the Si–Si bond forming bridge structures with the Si atoms without dissociating, where NH and atomic N form the most stable structures. Concerning the electronic properties, our results show that incorporated NH is the only structure which does not introduce trapping center at the interface. The structures involving NO and atomic N are acceptors, whereas that involving N₂ may be either a donor or an acceptor. The hydrogen passivation of the electrically active centers is also discussed. © 2004 American Institute of Physics. [DOI: 10.1063/1.1646466]

Oxynitride films have been extensively studied in the past years since they improve the reliability of metal-oxide-semiconductors gate insulators. The main benefits of incorporating nitrogen into ultrathin SiO₂ films are the reduction of gate leakage currents and the resistance to boron penetration.¹ The growth of ultrathin oxynitride films strongly depends on the reactant species (e.g., N₂O, NO, NH₃, N₂) and the technique used. Nitrogen can be incorporated into SiO₂ using either thermal oxidation and annealing or chemical and physical deposition methods. Thermal nitridation of SiO₂ in NO and N₂O generally results in a relatively low N concentration at the near-interface (Si–SiO₂) region.^{2,3} The N incorporation is commonly associated to the reaction of NO molecule with Si–Si bonds at the interface, after diffusing through the oxide.⁴ On the other hand, N incorporation via annealing in NH₃ is responsible for a relatively high N concentrations into the films.³ This method provides both near-interface and near-surface nitridation, suggesting different nitriding species derived from NH₃. More recently, higher N concentrations and controlled distributions have been attained by plasma assisted methods, typically using ions and radicals derived from N₂ and NH₃ as nitrogen sources.⁵ Although the control of both the density and the distribution of nitrogen into SiO₂ have been achieved at few-layer level, less is known about the early stages of the N-incorporation reactions at atomic level.

In this work the energetics and structural properties of near-interface nitrogen incorporation are studied from first-principles total-energy calculations. We have considered the N₂, NH, and NO molecules as well as atomic N as the precursor species, reacting with the Si–Si bonds in SiO₂ in order to simulate suboxide (Si³⁺) or near-interface N incorporation. Our calculations were performed in the framework of the density functional theory, using a basis set of numerical atomic orbitals as implemented in the SIESTA code.⁶ We have used a split-valence double- ζ basis set plus the polarization functions as well as standard norm-conserving pseudopotentials.⁷ For the exchange-correlation potential we

adopt the generalized gradient approximation.⁸ We used a 72-atom α -quartz supercell and the Γ point for the Brillouin zone sampling. The positions of all the atoms in the supercell were relaxed until all the force components were smaller than 0.05 eV/Å. We also consider neutral and singly charged species, where the neutrality of the cell is always maintained by introducing a compensating background charge. Spin-polarization effects, which are important for the correct description of atomic and molecular reaction processes in SiO₂,⁹ are included throughout the calculation.

We study the chemical reactions occurring when the nitriding species NO, NH, N₂, and atomic N approach the Si–Si bond in the otherwise perfect SiO₂ network. The Si–Si bond in SiO₂ is formed when an O atom is removed from the network characterizing an oxygen vacancy. This local geometry is close related to those found near the Si–SiO₂ interface.⁹ Hereafter, the incorporated species will be called [NO], [N₂], [NH], and [N]. For these reactions we only consider neutral species in their ground-state spin configurations. Initially, we study the structural properties of the nitriding species inside the largest interstitial site of a perfect SiO₂, exploring possible reactions that they may undergo with the network. Our results show that none of the species considered in this work react with the network, remaining at the interstitial sites. This suggests that neutral species would be diffusing species in SiO₂. However, when we put the species close to the Si–Si bond, they are quickly incorporated into the network forming the stable structures shown in Fig. 1. We now describe in details our results for each incorporated nitriding species.

The NO molecule shows two stable structures after reacting with the Si–Si bond. In the lowest-energy structure [NO], the N atom is threefold coordinated bonding with two Si atom, keeping the bond with the O atom, as shown in Fig. 1(a). Here, the Si–N and N–O bond lengths are 1.78 and 1.32 Å, respectively. The binding energy of NO, calculated as the difference in energy between the interstitial and incorporated configurations, is found to be 3.8 eV. Whereas, the binding energy of the O atom in the [NO] structure is 4.2 eV. Thus, it would be easier to remove the entire NO molecules

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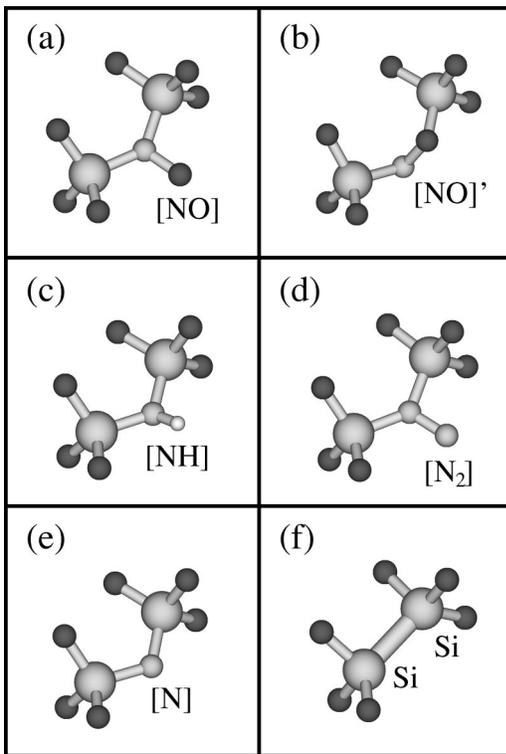


FIG. 1. Local equilibrium geometries for neutral nitriding species after reacting with Si-Si bond in SiO₂. (a) the most stable geometry for the incorporated NO. (b) the second stable geometry for the incorporated NO. (c)–(e) are the stable geometries for the incorporated NH, N₂, and atomic N, respectively. (f) the Si-Si bond or the suboxide region (Si³⁺) in SiO₂.

than the single O atom. Figure 1(b) shows the second stable geometry [NO]'. Here, NO is incorporated into the Si-Si bond forming a structure similar to the peroxy bridge of oxygens.^{9,10} This structure is 0.65 eV higher in energy than the most stable one. The Si-N, N-O, and O-Si bond lengths are 1.77, 1.40, and 1.71 Å, respectively. The energy barrier for the NO molecule to change from the metastable structure [NO]' to the most stable one [NO] is estimated to be 0.6 eV. The lowest-energy [NO] structure is an electrically active center, exhibiting a half-occupied energy level at 1.9 eV above the density-functional valence-band maximum (VBM) of α -quartz. The [NO] dangling bond may be passivated by capturing an H atom as recently suggested.¹¹ We find that the reaction involving the capture of an H atom from an interstitial H₂ molecule is endothermic with an energy cost of 0.78 eV. However, the [NO] passivation may occur by the capture of an interstitial H atom. In this case, the reaction is highly exothermic with an energy gain of 4.1 eV.

Figure 1(c) shows the equilibrium geometry for the NH after reacting with the Si-Si bond in SiO₂. We see that the N atom binds to both Si atoms forming the Si-N-Si structure, keeping the bond with the H atom. The Si-N and N-H bond lengths are 1.72 and 1.03 Å, respectively. The binding energy of the NH molecule is found to be 6.8 eV which indicates that this radical would be one of the most stable species for interface nitridation. We also found that the H atom is strongly bound to the N atom in [NH], having a binding energy of 4.6 eV.

The equilibrium geometry for the incorporated N₂ is shown in Fig. 1(d). The N₂ binding energy is found to be 1.2

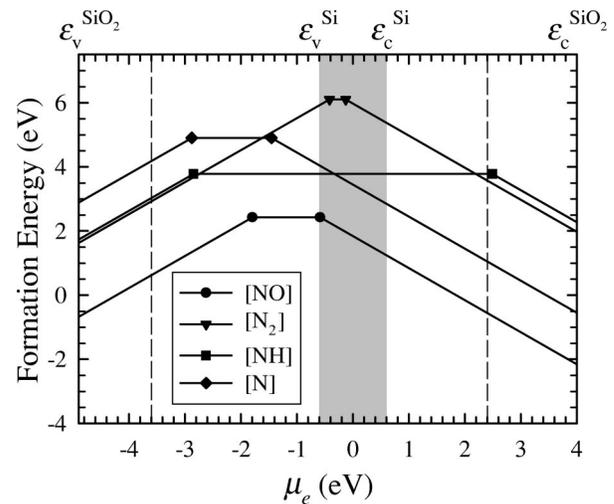


FIG. 2. Formation energies of the nitriding species after reacting with the Si-Si bond in SiO₂, as a function of the electron chemical potential (μ_e) in the energy gap of SiO₂. $\epsilon_v^{\text{SiO}_2}$ [$\epsilon_c^{\text{SiO}_2}$] is the experimental valence-band maximum (VBM) [conduction-band minimum (CBM)] of α -quartz. The dashed lines indicate the density-functional VBM and CBM and the shaded area represents the experimental band gap of bulk Si. The Si midgap is chosen as the zero energy of μ_e .

eV, relatively small as compared with the other nitriding species. This suggests that N₂ may be easily removed from the interface escaping from the SiO₂ film. Additionally, the [N₂] structure introduces an empty midgap level at 2.7 eV above the VBM of α -quartz.

For the N atom we also find a very stable structure after reacting with the Si-Si bond [Fig. 1(f)]. The binding energy of the N atom is found to be 6.5 eV. [N] shows a half-occupied energy level at 0.2 eV above the VBM of α -quartz. This dangling bond may be passivated by capturing an H atom from an interstitial H₂ molecule which dissociates after the contact with the [N] structure. We find that this reaction is exothermic with an energy gain of 0.82 eV, where the resulting equilibrium structure is similar to the [NH] structure [see Fig. 1(c)] plus an interstitial H atom. If the [N] passivation occurs by capturing an interstitial H atom, the reaction is highly exothermic with an energy gain of 5.0 eV.

The relative stability of incorporated nitriding species in SiO₂ in thermodynamic equilibrium is obtained by comparing their formation energies. As we are simulating the nitrogen incorporation at suboxide regions, i.e., close to the Si-SiO₂ interface, we consider the three most relevant charge states in order to address possible charge transfer between the incorporated species and the doped Si substrate. Therefore, the formation energies (E_f) are calculated as a function of the chemical potential of the nitriding species (μ_X) and the electron chemical potential (μ_e) as

$$E_f([X]^q, \mu_e) = E_t([X]^q) - E_t(\text{SiO}_2) + \mu_O - \mu_X + q\mu_e, \quad (1)$$

where $E_t([X]^q)$ is the total energy of the incorporated species X in the charge state q, $E_t(\text{SiO}_2)$ is the total energy of perfect α -quartz and μ_O the chemical potential of oxygen. μ_X and μ_O are fixed at the values of their stable gas phases. Our results for the formation energies of [NO], [NH], [N₂], and [N] are shown in Fig. 2. In the figure, the symbols indicate the transition states or the thermodynamics levels, Downloaded 08 Feb 2004 to 200.17.22.226. Redistribution subject to AIP license or copyright, see <http://apl.aip.org/apl/copyright.jsp>

whereas the slopes of the lines (positive, zero and negative) indicate the corresponding charge states. Following previous calculations,^{11,12} the transition states were aligned with respect to the experimental band-gap edges of α -quartz, by matching the calculated (+/-) transition state of the interstitial H atom in α -quartz with its measured value of 0.2 eV above the Si midgap,^{13,14} and by using the measured valence-band offset of the Si-SiO₂ interface of 4.3 eV.¹⁵ In Fig. 2 we also depict the experimental band gap of bulk Si where the Si midgap position is chosen to be the zero energy of μ_e .

As we are computing the energetics of the incorporated species close to the Si-SiO₂ interface, the variation of μ_e must be considered only in the energy range of bulk Si. Figure 2 shows that negatively charged [NO] is the most stable structure at the interface. The (0/-) transition state is found at 4.3 eV above the experimental SiO₂ valence-band maximum ($\epsilon_v^{\text{SiO}_2}$). This suggests that [NO] might capture an electron from the Si substrate characterizing an acceptor center at the Si-SiO₂ interface. The same behavior is found for [N] which might be another acceptor center at the interface. For the case of [N₂] we find both donor and acceptor character, where the (+/0) and (0/-) transition states are localized at $\epsilon_v^{\text{SiO}_2} + 4.5$ and $\epsilon_v^{\text{SiO}_2} + 4.8$ eV, respectively. The formation energy of [N₂] is approximately 2 eV higher in energy than [NO], suggesting that [N₂] would be the less stable structure at the interface. Finally, [NH] is found to be the only electrically inactive structure at the interface, having a relatively low formation energy. This suggests that the NH molecule would be the best choice among the considered nitriding species for interface nitridation.

In summary, we find that NH would be the most stable species for interface nitridation having a binding energy as high as 6.8 eV, where the N atom is typically threefold coordinated. NO would also be a very stable species at the interface having a binding energy of 3.8 eV. Our results agree well with the finding that NO diffuses through the oxide and reacts at the near-interface region where N is bound to two Si atoms and one O atom.⁴ However, NO does

not dissociate spontaneously after reacting with a Si-Si bond. N₂ may also be incorporated at the interface, forming a stable structure with the Si-Si bond. However, it has a relatively low binding energy of 1.2 eV. This suggests that N₂ may be easily removed from the interface. Atomic N does not react spontaneously with the SiO₂ network as commonly believed, suggesting that it would be a diffusing species in SiO₂. The binding energy of the incorporated N is 6.5 eV, resulting in a very stable species for interface nitridation. Concerning the electrical properties, our results show that NH is the only species that does not introduce a trapping center after being incorporated at the Si-Si bond. [NO] and [N] are acceptors whereas [N₂] may be a donor or an acceptor, depending on the Fermi level position. However, [N] and [NO] may be passivated by subsequent hydrogenation processes.

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